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Structural disorder produced in KH_2PO_4 by light-ion bombardment

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We study structural disorder produced in tetragonal KDP (KH_2PO_4) single crystals at room temperature by irradiation with MeV light ions. Results show that electronic energy loss plays a major role in the production of lattice defects in KDP. The effective diameters of ion tracks depend superlinearly on the electronic stopping power of energetic light ions. Structural lattice disorder is also accompanied by the formation of a network of cracks and blisters on the sample surface. Such irradiation-induced cracking and blistering typically evolves over extended periods of time (e.g., days) after bombardment, strongly affected by ion irradiation and sample storage conditions.

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Potassium dihydrogen phosphate, KDP (KH_2PO_4), and its deuterated form DKDP ($KD_{2x}H_{2(1-x)}PO_4$) are hydrogen-bonded ferroelectrics which find important applications as light frequency converters and Pockels cells in various laser systems.[1] These materials are particularly important for large-aperture high-power lasers since single-crystal KDP and DKDP can be conveniently grown with linear dimensions in the range of $50-100$ cm.[2]

However, there are still a number of challenges with the growth and processing of KDP. In particular, a relatively low threshold for the formation of laser-induced damage (LID) in these crystals effectively limits the maximum light intensities of large-aperture lasers.[2] It is generally believed that LID is due to localized absorption of high intensity light at some intrinsic lattice defects and/or impurities, resulting in ultrafast melting, material fracture, and plastic deformation.[2–5] The nature of such LID-initiating defects and impurities in KDP is currently unknown.[2] Hence, there is a need for systematic studies of stoichiometry, impurities, and defect structures in these materials.[2–6]

Ion-beam analysis techniques are very attractive for a range of structural and compositional characterization of solids.[7] However, these techniques typically use MeV light ions, which often produce undesirable lattice disorder in insulators. Thus, for a successful application of ion-beam analysis techniques for studies of impurities and defects in KDP, it is crucial to ascertain the lattice disorder produced in this material by ion bombardment. Ion irradiation studies of KDP are also important for a better understanding of fundamental defect-related properties of insulators and, particularly, hydrogen-bonded materials.

Ion-beam-defect processes in KDP are currently poorly understood. Previous studies have been limited to (i) observations of sample color changes produced by irradiation with several MeV light ion species,[8,9] (ii) optical absorption measurements after room-temperature 0.71 MeV ^{1}H ion irradiation,[9] and (iii) the observation of radiation-induced "spontaneous cleavage" after bombardment with 88 MeV ^{16}O ions.[8] In addition, Som et al.[10] have recently reported a Raman study of KDP irradiated with 1.5 MeV ^{4}He ions to fluences of 8.9×10^{14}, 1.7×10^{15}, and 3.5×10^{15} cm^{-2}, revealing evidence of some ion-beam-induced disordering as well as apparent loss of H. We are not aware of any previous reports on the effect of ion irradiation conditions on the formation of structural defects in KDP. Hence, in this letter, we present a study of structural disorder produced in KDP single crystals by different MeV light ions.

The z-cut [i.e., (001)-oriented] tetragonal KH_2PO_4 crystals used in this study were grown by a rapid growth method at LLNL, as described in detail elsewhere,[2] and polished with H_2O. The 4 MV ion accelerator (NEC, model 4UH) at LLNL was used for ion bombardment as well as for Rutherford backscattering/channeling (RBS/C) spectrometry analysis. For both ion irradiation and RBS/C analysis, the circular ion beam spot on the sample surface was $\sim$ 6 mm in diameter (normal incidence), and ion fluence was measured with a spinning wire technique described elsewhere.[11] All ion-beam experiments were done at room temperature. Table I gives the details of the ion irradiation conditions used. During irradiation, the surface normal of the samples was at an angle of $\sim 7^\circ$ relative to the incident beam axis. In cases of ^{1}H or ^{4}He ion irradiation, after each fluence increment, samples were characterized *in situ* by RBS/C with the same ions as used for bombardment incident along the [001] direction and backscattered into a detector at 164° relative to the incident beam direction. A beam of 2 MeV ^{4}He ions in the same scattering geometry was used for RBS/C analysis of disorder produced by 3.8 MeV ^{12}C ions. In the measurements of damage buildup curves, the total ion fluence used to acquire each RBS/C spectrum was $\lesssim 10^{13}$ cm^{-2}, which resulted in a negligible increase in the damage level for either ^{1}H or ^{4}He ion beam.

Figure 1 shows selected RBS/C spectra of KDP irradiated with 2 MeV He ions to different fluences. The RBS/C spectrum from the as-polished sample (the so-called virgin spectrum), also shown in Fig. 1, is characterized by a minimum RBS/C yield of better than $\sim 4\%$ (normalized to the random level), indicating good quality of the as-polished crystal. Figure 1 also clearly illustrates that, with increasing ion fluence, lattice damage rapidly builds up in the entire layer probed by 2 MeV He ions

TABLE I: Ion irradiation conditions used in this study. In all cases, irradiation was done at room temperature. Calculated valued of the projected ion range (R_p), electronic [$(dE/dx)_e$] and nuclear [$(dE/dx)_n$] stopping powers, effective diameters of ion tracks (d and d_T), and the number of overlaps (m) are also given. Note that d was determined from fitting experimental damage buildup curves by the damage overlap model, while d_T was calculated based on Tombrello's model.[12]

Ion	Energy (MeV)	R_p (μm)	Flux (10^{11} cm^{-2} s^{-1})	$(dE/dx)_e$ (eV/Å)	$(dE/dx)_n$ (10^{-3} eV/Å)	d (Å)	m	d_T (Å)
^{1}H	0.8	10.3	4	5.1	4	–	–	17
^{4}He	2.0	6.53	1 – 50	27.3	25	12.4	2	43
^{4}He	1.0	3.32	7	35.5	46	17.1	1	45
^{12}C	3.8	3.84	6	141.9	310	87.4	1	103

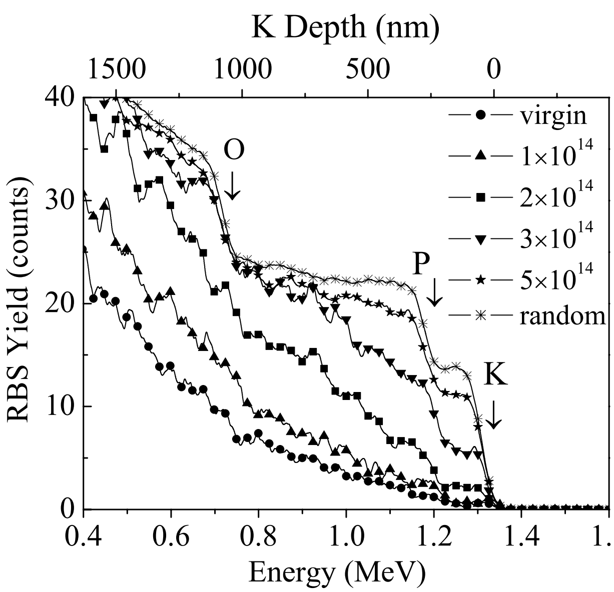

FIG. 1: Selected RBS/C spectra illustrating the buildup of structural disorder in KDP bombarded at 300 K with 2 MeV He ions with beam flux of $\sim 7\times10^{11}$ cm^{-2} s^{-1}. Implantation fluences (in cm^{-2}) are indicated in the figure. The positions of the surface peaks of K, P, and O are denoted by arrows.

(~ 1.5 μm).

The damage buildup behavior can be better illustrated by plotting the ion-fluence dependence of the RBS/C yield normalized to the random level. Figure 2(a) (symbols) shows such an ion fluence dependence of the normalized RBS/C yield[13] for each ion irradiation condition used in this study (see Table I). It is seen from Fig. 2(a) that, in the case of irradiation with He and C ions, structural disorder effectively accumulates up to complete disordering, as measured by RBS/C, at relatively low ion fluences ($\lesssim 10^{15}$ cm^{-2}). Figure 2(a) also shows that the damage buildup curves shift toward lower fluences with increasing ion stopping power (which is also given in Table I).[14,15]

Damage buildup curves can often be described by the well-known defect overlap model.[16] This model takes into account a spatial overlap of regions with an incompletely disordered crystal structure. It is assumed that an m-fold spatial overlap of incompletely disordered regions with an effective diameter d is required for complete lattice disordering. Solid lines in Fig. 2(a) show the best fits to experimental data based on the damage overlap model.[16] The values of parameters m and d obtained from such a fitting procedure are given in Table I, suggesting that single or double spatial overlap of ion tracks is necessary to disorder the KDP lattice with He and C ions. We have also found that a variation in the flux of 2 MeV ^{4}He ions from 1×10^{11} to 5×10^{12} cm^{-2} s^{-1} has a negligible effect on the damage buildup. Such a negligible beam flux effect indicates that the stabilization of defect structures within ion tracks occurs much faster (or much slower) than the average time interval between the generation of ion tracks that spatially overlap.

The buildup of structural disorder revealed in Figs. 1 and 2(a) is a result of electronic energy loss $(dE/dx)_e$ (i.e., the excitation of the electronic subsystem) rather than nuclear energy loss $(dE/dx)_n$ (i.e., ballistic atomic displacements) by energetic light ions. Indeed, Table I shows that, for the MeV light ions used in this study, $(dE/dx)_e$ is significantly larger than $(dE/dx)_n$. In addition, calculations with the TRIM code[15] show that bombardment with 2 MeV ^{4}He ions to a fluence of 10^{15} cm^{-2} generates $\sim 5\times10^{-4}$ displacements per atom in the KDP lattice near the sample surface, whereas Fig. 2(a) clearly indicates complete lattice disordering for such bombardment conditions. The conclusion that $(dE/dx)_e$ plays a major role in the damage production in KDP under MeV light-ion bombardment is further supported by the fact that the damage buildup in this material is only slightly (within $\sim 10\%$) dependent on whether ion irradiation is done in channeling or random direction. Indeed, in contrast to the case of $(dE/dx)_e$, $(dE/dx)_n$ is significantly different for channeling and random ion irradiation conditions.[7]

Figure 2(b) shows a double logarithmic plot of the dependence of d on $(dE/dx)_e$. It is seen from Fig. 2(b) that such a dependence can be fitted with a straight line with a slope of 1.18 ± 0.01, indicating a slightly superlinear character.[17] Extrapolation of the straight line in Fig. 2(b) to the $(dE/dx)_e$ value for 0.8 MeV ^{1}H ions (see Table I) gives a d value of ~ 1.7 Å. This value is consistent with

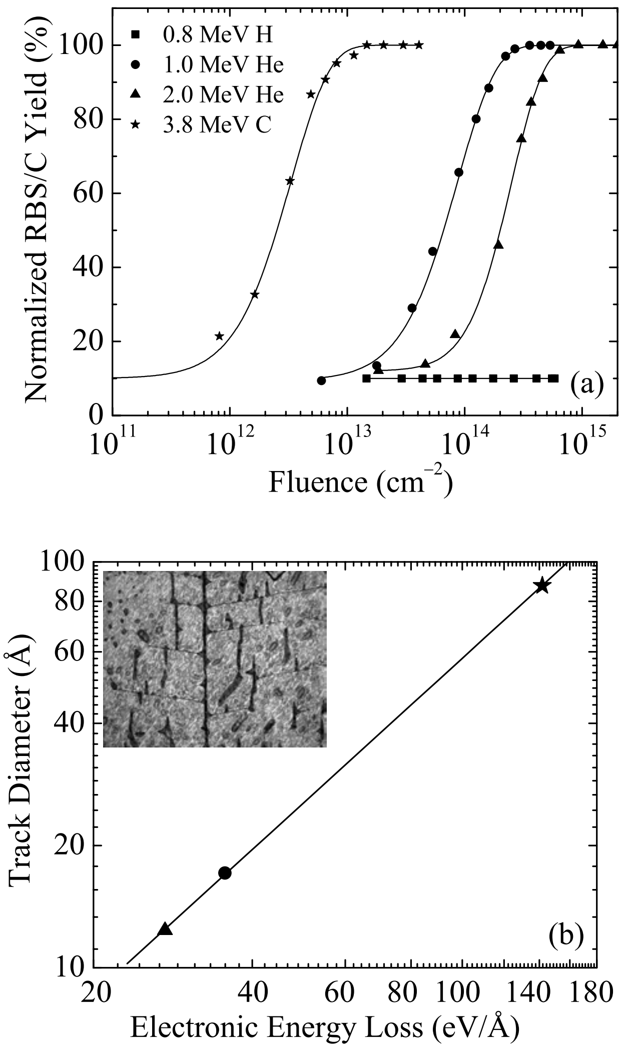

FIG. 2: (a) Symbols: The ion fluence dependence of the RBS/C yield, normalized to the random level, extracted from spectra for different irradiation conditions, as indicated in the legend. Curves: results of calculations based on the damage overlap model. (b) The dependence of the effective track diameter on electronic energy loss. The same symbols as in (a) are used for different irradiation conditions. The straight line with a slope of 1.18 ± 0.01, representing the best fit, is also shown. The inset in (b) shows an optical micrograph of KDP irradiated at 300 K with 2 MeV He ions to a fluence 10^{14} cm^{-2}. The image was taken ~ 2 days after ion irradiation. The horizontal field width of the image is 2.75 mm.

the experimental result from Fig. 2(a) that bombardment with 0.8 MeV H ions up to the maximum fluences used in this study ($\sim 10^{15}$ cm^{-2}) produces negligible stable lattice disorder, as measured by RBS/C. Indeed, calculations based on the defect overlap model[16] show that, even in the case of single overlap with $d = 1.7$ Å, ion fluences $\gtrsim 10^{15}$ cm^{-2} would be needed to produce disorder levels measurable by RBS/C.

Several physical processes can, in principle, be responsible for the MeV-light-ion-induced formation of tracks revealed in this study. These processes include (i) radiolysis, (ii) the thermal spike, (iii) Coulomb explosion,[18] and (iv) material instability at high levels of electronic excitation.[19] However, based on the experimental data available, it is difficult to ascertain which physical process plays the major role in defect formation in KDP. As an example, the last column in Table I shows track diameters d_T calculated based on an empirical model for track formation in insulators developed by Tombrello.[12,20] This analytical model has successfully been used to predict track diameters in a number of (mostly inorganic) insulators.[12] However, a comparison of d (measured) and d_T (calculated) from Table I shows that Tombrello's model cannot describe the superlinear dependence of d on the electronic stopping power in KDP revealed in the present study. This could be attributed to the complexity of defect processes in hydrogen-bonded materials, such as KDP, and the limitations of Tombrello's model discussed in detail in Ref. 12. Hence, at the moment, understanding physical mechanisms of ion track formation in KDP should await further systematic studies.

Finally, the complexity of defect processes in KDP is further illustrated in the inset in Fig. 2(b), showing an optical microscopy image of KDP irradiated with 2 MeV ^{4}He ions to a fluence of 10^{14} cm^{-2}. This image of the irradiated sample, taken $\sim$ 2 days after storage at ambient conditions, clearly illustrates the development of an irradiation-induced network of near-surface cracks and blisters. Such cracking and blistering, attributed to irradiation-induced stress, is consistent with previous observations of surface color changes and "spontaneous cleavage" in ion-irradiated KDP.[8,9] However, we have found that the formation of cracks and blisters typically proceeds over extended periods of time (such as days) after ion irradiation and strongly depends on irradiation parameters as well as the ambient conditions (such as temperature and humidity) during sample storage. These interesting effects currently require additional systematic studies.

In conclusion, ion-beam-produced structural disorder in KDP has been studied by RBS/C. Results have shown that KDP exhibits a complex ion-beam damaging behavior, with electronic energy loss being responsible for defect production. This study could have important implications for establishing ion irradiation parameters required to perform a nondestructive ion-beam analysis of KDP nonlinear crystals and other hydrogen-bonded materials.

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